Spal

A reactor which is used as a steam and CO₂ hydrocarbon reforming, steamalcohol reforming, water gas shift, and dehydrogenation reactor, which consists of a farouter impermeable hollow tubular cylinder which nests two more concentric hydrogen permeable tubular cylinders, having the inner permeable one to be nested within the outer remeable, with the inner permeable cylinder to be filled with catalyst particles, < with turbular type heaters to be located within the catalyst zone, and run parallel to the inner cylindrical axis, with the catalyst in pellet or particle form to be a reforming, water gas shift andehydrogenation catalyst depending on the feedstocks fed in the inlet of the reactor and the type of reactions conducted within the catalytic zone, moreover, with hydrogen to be removed via permeation along the inner membrane tube, wherein the /o membrane is made by a metal, metal alloy, non-porous inorganic or carbon material, with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols and non-permeate hydrogen to be rejected by the membrane and exit through the main outlet of the inner tube, with the permeate hydrogen to be diluted by a carrier gas flowing along the annulus between the inner and outer permeable tubes and to be further removed through 15 permeation along the outer permeable membrane tube, wherein the outer membrane is made by a metal, non porous inorganic, or carbon material, so that second permeated stream contains pure hydrogen only, with the annular space between the outer membrane tube and the far-outer impermeable tube which receives final permeate hydrogen to contain a selective catalyst, wherein permeate hydrogen reacts with a sweep component 20 flowing through the inlet of this annular space, parallel to the outer membrane tube, in an exothermic type reaction, with the heat generated by the exothermic reaction in the mostouter catalytic zone to be transferred via the radial direction into the main catalytic reaction zone of the inner memorane tube thus providing for part of the heat load necessary to drive the endothermic catalytic reactions in the inner membrane tube, with 25 the main heating load of this inner catalytic zone to be achieved via heat transfer from tubes flowing gas, arranged symmetrically around the reactor axis and operated in the combustion regime by flowing waste type hydrocarbons or hydrocarbon-hydrogen mixtures mixed with oxygen or air, also by flowing unreacted hydrocarbons and carbon monoxide post-reaction species, and any of their mixtures, exiting from the inner30 membrane tube outlet, and recovered in the downstream of the reactor through various > (2 separation processes including separation through membrane permeation, and by having these mixtures to be recycled as fuel into the inlet of these heating tubes to support combustion and heat provision in the surrounding inner catalytic zone, with the sweep component, which reacts with the hydrogen permeated from the outer membrane tube, to 35 be

an unsaturated hydrocarbon such as an alkene or alkyne for hydrogenation to a saturated hydrocarbon,

also to be carbon monoxide for hydrogenation to methanol or gasoline hydrocarbons,

also to be nitrogen for hydrogenation to ammonia

also to be an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon,

also to be an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction with hydrogen to a corresponding saturated component,

also to be an alkyl or aryl halide for reduction with hydrogen to a corresponding non-halogene component,

\ also to be a nitroalkane or aromatic nitro compound for reduction with hydrogen

to a corresponding primary amine.

- 2. The reactor assembly and process of claim 1, wherein annular space enclosed between the outer permeable membrane tube and the far-outer impermeable metal tube is empty and the permeate pure hydrogen through outer membrane tube is used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.
- 3. The process of chaim 1 wherein the inner membrane tube is made by a porous inorganic or inorganic-metal membrane material with hydrogen to permeate through the membrane, and carbon monoxide, carbon dioxide, steam, reactant and product hydrocarbons and alcohols to permeate also through the membrane in a lesser degree, with hydrogen only to permeate through the outer metal, non-porous inorganic or carbon membrane tube and with the remaining non-permeate species to exit through the reject outlet of the annular space created between the two membrane tubes either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate pure hydrogen through the outer membrane to be used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.
- The process of claim 1 as applied to carbon dioxide hydrocarbon reforming and dehydrogenation reactions, wherein the inner membrane tube is made by a porous inorganic or inorganic-metal material with hydrogen to permeate through the membrane, and carbon monoxide, carbon dioxide, reactant and product hydrocarbon species, to permeate also through the membrane in a lessel degree, and with the outer membrane tube to be made by an organic polymer\membrane which withstands high temperatures and is permselective to both hydrogen and carbon dioxide species, with hydrogen and carbon dioxide in the reforming reaction case or hydrogen only in the dehydrogenation case to permeate through the outer membrane, and with the remaining non-permeate species to exit through the reject outlet of the annular space created between the two membrane tubes, either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate through the outer membrane hydrogen and carbon dioxide mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, and in the corresponding case wherein hydrogen only is the permeate through the outer membrane tube, the permeate hydrogen to be used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of

proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

A reactor which is used as a steam and CO₂ hydrocarbon reforming, steam-alcohol reforming, water gas shift, and dehydrogenation reactor, which consists of a most outer non-permeable tubular cylinder which is hollow in the center and nests two more concentric hollow membrane tubular cylinders, a next-inner one and a most-inner one, which are both made by permeable materials with the annular space between most-outer and next-inner dylinders to contain a metallic catalyst in the form of pellets or particles, with the catalyst to be a reforming, water gas shift or dehydrogenation catalyst depending on the feedstocks/fed in the inlet of the annular catalytic zone and the type of reactions conducted within the catalytic zone, with the next-inner cylinder to nest also a concentric most-inner hollow membrane cylinder, with next-inner cylinder to be made by a metal, metal alloy, non-porous inorganic, or carbon material which is permeable only to hydrogen, with product hydrogen from the catalytic reaction zone to permeate through the lateral membrane\surface of next-inner cylinder with carbon monoxide, carbon dioxide, steam, hydrocarbons, alcohols and non-permeate hydrogen to be rejected by the next-inner membrane and exit through outlet fitting ports located by the end of the catalytic zone, with permeate hydrogen flowing along the annular zone between nextinner and most-inner cylinders to be diluted by a carrier gas flowing along the same annulus and to be further removed via permeation across the most-inner permeable membrane tube, wherein most-inner membrane tube is made by metal, metal-alloy, nonporous inorganic or carbon materials, so that secondly permeated stream flowing inside most-inner membrane tube contains only pure hydrogen, with the most-inner membrane tube to contain a selective catalyst in form of particles or pellets, wherein permeate hydrogen reacts with a sweep component flowing through an inlet port of the most-inner membrane tube in an exothermic type\reaction, with the heat generated by the exothermic reaction in the most-inner catalyst zone to be transferred into the main catalytic reaction zone enclosed between most-outer and next-inner hollow cylinders, thus providing for part of the heat load necessary to drive the endothermic catalytic reactions occurring in this zone, with the main heating of the overall cylindrical assembly and main catalytic zone to be achieved by heat transfer coming from combustion of gases, including combustion of waste type hydrocarbons and hydrocarbon-hydrogen mixtures mixed with oxygen or air, also of unreacted hydrocarbons and carbon monoxide post-reaction species and any of their mixtures exiting from the corresponding reaction outlet port, which are recovered in the downstream of the reactor through various separation processes including separation through membrane permeation and recycled as fuel flowing along the external side of the most-outer impermeable cylinder to support combustion and heat provision in enclosed main catalytic zone, with the sweep component which reacts with the hydrogen permeated in the most-inner membrane tube, to be

an unsaturated hydrocarbon such as an alkene or alkyne for hydrogenation to a saturated hydrocarbon,

also to be carbon monoxide for hydrogenation to methanol or gasoline hydrocarbons,

also to be nitrogen for hydrogenation to ammonia, also to be an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon,

also to be an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction

with hydrogen to a corresponding saturated component,

also to be an alkyl or aryl halide for reduction with hydrogen to a corresponding

non-halogene component,

also to ba a nitroalkane or aromatic nitro compound for reduction with hydrogen to a corresponding primary amine.

- The reactor assembly and process of claim 5, wherein most inner membrane tube 6. is empty and the pure permeate hydrogen within this tube is used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons, and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.
- The process of claim 5 wherein next-inner hollow cylinder is made by a porous 7. inorganic or inorganic-metal membrane, with hydrogen to permeate through the membrane, and carbon monoxide, carbon dioxide, steam, reactant and product hydrocarbons, alcohols, to permeate also through the membrane in a lesser degree, with hydrogen only to permeate through the most-inner metal, metal alloy, non-porous inorganic, or carbon membrane tube and with the remaining non-permeate species, to exit through the reject outlet of the annular space created between the next-inner and most-inner cylinders, either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate through the inner membrane tube, pure hydrogen product, to be used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.
- The process of claim 7, as applied to carbon dioxide hydrocarbon reforming and 8. dehydrogenation reactions only, wherein the most-inner membrane tube is made by an organic polymer membrane which withstands high temperatures and is permselective to both hydrogen and carbon dioxide species, which permeate through the most-inner membrane tube, with the remaining non-permeate species to exit through the reject outlet of the annular space created between the next-inner and most-inner membrane tubes, either as it is mixture or after mixing with another carrier gas flowing through the same annular space, with the permeate through the most-inner membrane tube hydrogen and carbon dioxide mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, and in corresponding case wherein hydrogen only permeates through the most-inner membrane tube, the permeate hydrogen to be used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate,\solid oxide and phosphoric acid types.

A reactor which is used as a carbon dioxide hydrocarbon reforming and dehydrogenation reactor, which consists of multiple membrane tubes nested within an outer non-permeable hollow metal cylinder which also contains a catalyst in particle or pellet form, with the catalyst to be a reforming or dehydrogenation catalyst depending on the feedstocks fed in the inlet of the catalytic zone and the type of reactions conducted within the catalytic zone, with the multiple membrane tubes to be made by organic type polymer membrane material which withstands high temperature and is permselective to both hydrogen and carbon dioxide species which permeate into the multiple inner membrane tubes from the catalytic zone, with the remaining non-permeate carbon monoxide, product and reactant hydrocarbons and non-permeate hydrogen and carbon dioxide to be rejected by the polymer membrane tubes and exit through outlet fitting ports located by the end of the catalyst zone, with permeate hydrogen and carbon dioxide mixture from the reforming reaction or permeate hydrogen only from the dehydrogenation reaction, which are flowing in the inner side of the membrane tubes either as unmixed gas or as a mixture with another carrier component flowing through a common inlet via all the membrane tubes, to be continuously removed via a common impermeable metal shell which is interconnected with all the membrane tubes and sealed from the gases flowing out of the catalytic reaction zone of the outer cylinder, with the multiple organic polymer membrane tubes to contain a selective catalyst in form of particles or pellets wherein mixture of permeate hydrogen and carbon dioxide react to produce methanol or carbon monoxide or methane, and alternatively, permeate hydrogen only reacts with a sweep component flowing through all membrane tubes via a common inlet, in an exothermic type of reaction, with the heat generated by the exothermic reaction in the catalytic zone enclosed within the tubes to be transferred in the outer catalytic reaction zone, thus providing for part of the heat load necessary to drive the occurring endothermic reforming or dehydrogenation reactions, with the main heating of the outer cylinder and enclosed catalytic zone to be achieved via heat transfer from combustion of gas flowing in external side of the outer cylinder, including combustion of waste type hydrocarbons and hydrocarbon-hydrogen mixtures mixed with oxygen or air, including unreacted hydrocarbons and carbon monoxide post-reaction species and any of their mixtures exiting from the outer catalytic zone via suitable outlet fitting ports, which gases are recovered in the downstream of the reactor through various separation processes including separation through membrane permeation and recycled as fuel along the external side of the outer cylinder to support combustion and heat provision in the enclosed outer catalytic zone, with the sweep component which reacts with the hydrogen permeated in the inner membrane tubes, to be

an unsaturated hydrocarbon such as an alkene or alkyne for hydrogenation to a

saturated hydrocarbon,

also to be carbon monoxide for hydrogenation to methanol or gasoline hydrocarbons,

also to be nitrogen for hydrogenation to ammonia,

also to be an aromatic hydrocarbon for reduction with hydrogen to a non-aromatic hydrocarbon.

Cap (3)

also to be an unsaturated alcohol, phenol, aldehyde, ketone, or acid for reduction with hydrogen to a corresponding saturated component,

also to be an alkyl or aryl halide for reduction with hydrogen to a corresponding

non-halogene component,

also to be a nitroalkane or aromatic nitro compound for reduction with hydrogen to a corresponding primary amine.

- 10. The reactor assembly and process of claim 9, wherein the inner membrane tubes are empty and the hydrogen and carbon dioxide mixture or the hydrogen gas only which permeate in these tubes and recovered in the downstream is used as feed in various consecutive applications including hydrogenation reactors for methanol, gasoline hydrocarbons and ammonia synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.
- 11. The process of claim 1, as applies to the steam and CO₂ hydrocarbon reforming reactions, with H₂ and CO to be produced via the reversible hydrocarbon steam reforming, hydrocarbon CO₂ reforming, and water gas shift reactions, with the final permeate stream to contain pure hydrogen product, permeated through the far outer membrane tube, and with the reject exit stream from the reactor which contain carbon monoxide product, non-permeate hydrogen product, unreacted hydrocarbon, carbon dioxide and unreacted and produced steam to be passed through a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

organic polymer membrane,

inorganic membrane,

composite inorganic-metal-organic membrane,

composite organic-inorganic membrane,

composite organic-metal membrane

which all materials are permselective to H_2 and CO_2 and separate these two species in permeate stream from the unreacted hydrocarbon and carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the H_2 and CO_2 permeate product mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

chemical synthesis

and fuel type reactions

either as a mixture or after the CO2 condensation and removal, as pure hydrogen, either

as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

(g)

12. The process of claim 5, as applies to the steam and CO₂ hydrocarbon reforming reactions, with H₂ and CO to be produced via the reversible hydrocarbon steam reforming, hydrocarbon CO₂ reforming, and water gas shift reactions, with the final permeate stream to contain pure hydrogen product, permeated through the most inner membrane tube, and with the reject exit stream from the reactor which contains carbon monoxide and non-permeate hydrogen product, unreacted hydrocarbon, carbon dioxide and unreacted and produced steam to be passed through a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

organic polymer membrane,

inorganic membrane

composite inorganic metal-organic membrane,

composite organic-inorganic membrane,

composite organic-metal membrane,

which all materials are permselective to H₂ and CO₂ and separate these two species in permeate stream from the unreacted hydrocarbon and carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the H₂ and CO₂ permeate product mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

chemical synthesis

and fuel type reactions

either as a mixture or after the CO₂ condensation and removal, as pure hydrogen, either

as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

13. The process of claim 9, as applies to the CO₂ hydrocarbon reforming reaction, by feeding CO₂ and a hydrocarbon or CO₂ and a mixture of hydrocarbons in the catalytic reaction zone, with H₂ and CO to be produced via the reversible hydrocarbon CO₂ reforming and water gas shift reactions, with the final permeate stream to contain hydrogen product, carbon dioxide reactant and traces of steam which may also permeate through the multiple inner polymer membrane tubes, with the steam to be removed by passing the stream through a bed of moisture adsorbing particles, with the remaining hydrogen and CO₂ mixture to be used in consecutive applications, and with the reject exit stream from the reactor which contains carbon monoxide product, non-permeate hydrogen product, non-permeate unreacted carbon dioxide, unreacted hydrocarbon and traces of product steam to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

organic polymer membrane,

-inorganic membrane

composite in organic-metal-organic membrane,

composite organic-inorganic membrane,

composite organic-metal membrane,

which all materials are permselective to H_2 and CO_2 and separate these two species in permeate stream from the unreacted hydrocarbon and carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the H_2 and CO_2 permeate product mixture to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

chemical synthesis

and fuel type reactions either as single stream or as combined stream after its combination with the hydrogen and CO₂ stream permeated from the first permeable reactor.

14. The process of claim 12, wherein the membrane permeator which follows the permeable reforming reactor is made by a metal, metal alloy, non-porous inorganic, or carbon membrane which is permselective only to hydrogen and separate hydrogen in permeate stream from the unreacted hydrocarbon, carbon dioxide, and product carbon monoxide, which all exit from the non-permeate side of the permeator as a reject stream, with the recovered hydrogen in permeate stream to be used either directly, or after combination with the permeate hydrogen recovered from the first permeable reactor, in

chemical synthesis, including\methanol, gasoline hydrocarbons and ammonia,

in fuel type reactions \ including as hydrogen feed, in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

15. The process of claim 12, with the reject stream from the permeator containing unreacted hydrocarbon and CO to enter into a consecutively placed steam reformer to react with steam over a bed of metallic catalyst via the steam reforming and water gas shift reactions and be converted into H₂ and CO₂ products, having this exit stream from last reformer to condense its unreacted steam by passage through a heat exchanger and by generating new steam in other side of the heat exchanger which is used as feed in the inlet of this last reformer, having the final exit dry mixture of H₂ and CO₂ from the heat exchanger to be combined with the permeate from the membrane permeator H₂ and CO₂ stream, to make one combined stream of H₂ and CO₂ to be used for methanol synthesis and as feed in molten carbonate fuel cells, also in other

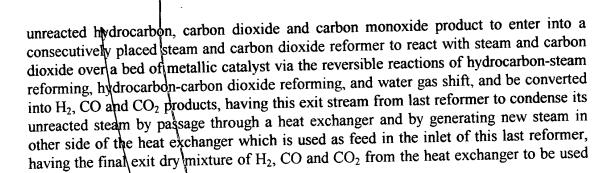
chemical synthesis

and fuel type reactions

either as a mixture or after the CO₂ condensation and removal, as pure hydrogen, either as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

16. The process of claim 14, with the reject stream from the permeator containing



chemical synthesis,

and as fuel

for

either as it is mixture, or after the CO2 condensation and removal, as pure synthesis gas mixture of hydrogen and carbon monoxide, either

as single stream or

as combined stream

after its combination with the hydrogen stream permeated from the permeator and the first permeable reforming reactor.

The process of daim 12 wherein the hydrocarbon is a single constituent or a 17. mixture of constituents of the following components:

methane.

ethane,

propane,

n-butane,

i-butane,

methanol,

ethanol,

propanol,

butanol,

natural gas rich in methane,

coal gas rich in methane,

landfill gas rich in methane,

flue gas rich in methane,

and wherein the combined hydrocarbon and carbon dioxide gas mixture is substituted by:

a CH₄ and CO₂ mixture,

acidic natural gas rich in CH4 and CO2,

coal gas rich in CH₄ and CO₂,

landfill gas rich in CH₄ and CO₂,

other refinery and flue gas mixtures rich in CH_4 and CO_2 .

The process of claim 12 wherein the membrane in permeator is made from an 18. organic polymer or composite or copolymer of organic polymers selected from the group of

_polyimides,

polycarbonates,

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polysulfones,
polybenziimidazoles,
polyphosphazenes,
polyamides,
polystyrenes,
polycaprolactams,
parylenes,
polyvinyl halides,
polyagetates,
polysiloxanes
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or from inorganic-organic composite materials made by a mixture of one or more of the above polymers with one or more of the following ceramic oxides:

alumina (Al₂O₃), titania (TiO₂), silica (SiO₂), zirconia (ZrO₂).

19. The process of claim 9 wherein the inner membrane tubes within the reactor are made from an organic polymer or composite or copolymer of organic polymers selected from the group of

polyimides, polycarbonates, polysulfones, polybenziimidazoles, polyphosphazenes, polyamides, polystyrenes, polycaprolactams, parylenes, polyvinyl halides, polyacetates, polysiloxanes.

20. The process of claim 12 wherein the permeator following the first permreactor is replaced by a catalytic permreactor to reactively process the exit stream from the first permreactor which is rich in CO product, by conducting the water gas shift reaction with H₂ and CO₂ products, also in case of low conversion in the first permreactor wherein first permreactor exit stream contains significant amounts of unreacted methane and carbon dioxide by conducting as well in following catalytic permreactor the reversible methane steam reforming and methane carbon dioxide reforming reactions together with the water gas shift reaction over a bed of metallic catalyst with main products H₂, CO and with the following membrane permreactor to be made by one of the following materials:

metal or metal alloy membrane, non-porous inorganic membrane, carbon membrane

which all materials are permselective to H_2 and separate H_2 only in permeate stream of the permreactor from the unreacted hydrocarbon, steam, CO_2 , and CO which all exit from the non-permeate side of the permreactor as a reject stream which is recycled as feed into the first permreactor if it is rich in CO_2 , or in the second permreactor if it is rich in CO, with the permeate H_2 to be used in

chemical synthesis and fuel type reactions

either, as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

21. The process of claim 11 wherein the permeator following the first permreactor is replaced by a catalytic permreactor to reactively process the exit stream from the first permreactor which is rich in CO product, by conducting the water gas shift reaction with H_2 and CO_2 products, also in case of low conversion in the first permreactor wherein first permreactor exit stream contains significant amounts of unreacted methane and carbon dioxide by conducting as well in following catalytic permreactor the reversible methane steam reforming and methane carbon dioxide reforming reactions together with the water gas shift reaction over a bed of metallic catalyst with main products H_2 , CO and with the following membrane permreactor to be made by one of the following materials:

metal or metal alloy membrane, non-porous inorganic membrane,

carbon membrane

which all materials are permselective to H_2 and separate H_2 only in permeate stream of the permreactor from the unreacted hydrocarbon, steam, CO_2 , and CO which all exit from the non-permeate side of the permreactor as a reject stream which is recycled as feed into the first permreactor if it is rich in CO_2 , or in the second permreactor if it is rich in CO, with the permeate H_2 to be used in

chemical synthesis

and fuel type reactions

either, as single hydrogen stream of

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

- 22. The process of claim 12 wherein the feed stream into first permreactor consists of a hydrocarbon and carbon dioxide or a mixture of hydrocarbons and carbon dioxide, reformed over a bed of metallic catalyst via the reversible CO₂ hydrocarbon reforming and water gas shift reactions to produce H₂ and CO products.
- 23. The process of claim 11 wherein the feed stream into first permreactor consists of a hydrocarbon and carbon dioxide or a mixture of hydrocarbons and carbon dioxide, reformed over a a bed of metallic catalyst via the reversible CO₂ hydrocarbon reforming and water gas shift reactions to produce H₂ and CO products.



24. The process of claim 12 wherein the combined H₂ and CO₂ product mixture from the permeator is used:

(a) \for direct methanol synthesis via the reaction: CO₂+3H₂=CH₃OH+H₂O,

(b) for direct feed in molten carbonate fuel cell (MCFC) units for electricity generation via the overall electrochemical reaction: $H_2+CO_2+1/2O_2$ (cathode) --- H_2O+CO_2 (anode),

(c) for other CO_2 and H_2 direct combination reaction, moreover, after the removal of CO_2 by condensation, the generated pure H_2 is combined with pure H_2 coming out of the first reforming reactor and used:

(d) as fuel feed in hydrogen based fuel cell units including molten carbonate, solid oxide, proton exchange, alkaline, phosphoric type,

(e) as fuel feed in gas turbines, conventional and jet type gas engines,

- (f) as synthesis reactant in consecutive hydrogenation reactors including these for methanol, ammonia and gasoline hydrocarbon synthesis, also these for saturation of unsaturated hydrocarbons including alkenes to alkanes, alkynes to alkenes to alkanes, also these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides, and these for reduction of nitroalkanes and aromatic nitro compounds into corresponding primary amines.
- 25 The process of claim 11 wherein the combined H₂ and CO₂ product mixture from the permeator is used:

for direct methanol synthesis via the reaction: CO₂+3H₂=CH₃OH+H₂O,

(b) for direct feed in molten carbonate fuel cell (MCFC) units for electricity generation via the overall electrochemical reaction: $H_2+CO_2+1/2O_2$ (cathode) --- H_2O+CO_2 (anode),

(c) for other CO_2 and H_2 direct combination reaction, moreover, after the removal of CO_2 by condensation, the generated pure H_2 is combined with pure H_2 coming out of the first reforming permreactor and used:

(d) as fuel feed in hydrogen based fuel cell units including molten carbonate, solid oxide, proton exchange, alkaline, phosphoric type,

(e) as fuel feed in gas turbines, conventional and jet type gas engines,

- (f) as synthesis reactant in consecutive hydrogenation reactors including these for methanol, ammonia and gasoline hydrocarbon synthesis, also these for saturation of unsaturated hydrocarbons including alkenes to alkanes, alkynes to alkenes to alkanes, also these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides, and these for reduction of nitroalkanes and aromatic nitro compounds into corresponding primary amines.
- 26. The process of claim 12 wherein the feed stream into the first permreactor consists only of carbon monoxide and steam $(H_2Q(g))$ mixture, reacting over a bed of metallic catalyst to produce H_2 and CO_2 via the water gas shift reaction alone, with hydrogen to permeate through the most-inner membrane tubes and with the remaining

components including unreacted carbon monoxide, steam, carbon dioxide product and non-permeate hydrogen to exit through the reject stream of the outer cylinder.

- The process of claim 26 with the reject stream from the permeator containing 27. non-permeate unreacted CO to be recycled into the inlet of first water gas shift permreactor for continuous water gas shift reaction into the main outer catalytic zone.
- The process of claim 26 with the reject stream from the permeator containing 28. non-permeate unreacted CO to enter into a consecutive placed water gas shift reactor to react with steam over a bed of metallic catalyst via the water gas shift reaction and be converted into H2 and CO2 product, having the exit stream from last shift reactor to condense its unreacted steam by passage through a heat exchanger and by generating new steam in the other side of the heat exchanger to be used as feed in the inlet of this last shift reactor in an autothermic type operation, having the final exit dry mixture of H₂ and CO₂ from last/heat exchanger to be combined with the permeate from the membrane permeator H₂ and CO₂ stream, to make a combined stream for use as feed in methanol synthesis and molten carbonate fuel cells, also in other

chemical synthesis and fuel type reactions either as it is mixture or after the CO2 condensation and removal, as pure hydrogen, either

as single hydrogen stream or

as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reactor.

The process of claim, 5, as applies to dehydrogenation reactions of alkanes, with 29. the feed to consist of pure or mixture of alkanes which are saturated hydrocarbons and react in the catalytic zone of the permreactor, with hydrogen and unsaturated alkenes to be produced via reversible dehydrogenation reactions, with the final permeate stream to contain pure hydrogen product permeated through the most-inner membrane tube and with the exit reject stream from the permreactor which contains product alkenes and nonpermeate hydrogen and unreacted alkanes, to be passed through a heat exchanger to reduce its temperature by generating steam in other side of the exchanger which is used as feed into any steam requiring process with the exit from the heat exchanger alkenes, alkanes and hydrogen mixture to be entered into a membrane permeator wherein the membrane is made by one of the following materials:

organic polymer membrane, inorganic membrane, composite inorganic metal-organic membrane composite inorganic organic membrane composite metal-organic membrane metal or metal alloy membrane non-porous inorganic membrane carbon membrane

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which all materials are permselective to hydrogen only, and separate hydrogen in permeate stream from the unreacted alkanes and product alkenes, which exit from the non-permeate side of the permeator as a reject stream to be used for

polyolefin synthesis in consecutive polymerization reactors,

oxygenated compound synthesis in consecutive synthesis reactors,

including ethylene glycol, ethylene oxide, propylene glycol, propylene oxide, ethanol, propanol, isopropanol, with the hydrogen product recovered in the permeate stream of the permeator to be used as single hydrogen stream or as combined hydrogen stream after its combination with the hydrogen stream permeated through the first permeable reactor, in

chemical synthesis

and in fuel type reactions,

including use as feedstock to hydrogenation reactors for methanol, ammonia, and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

30. The process of claim 1 as applies to dehydrogenation reactions of alkanes, with the feed to consist of pure or mixture of alkanes which are saturated hydrocarbons and react in the catalytic zone of the permreactor, with hydrogen and unsaturated alkenes to be produced via reversible dehydrogenation reactions, with the final permeate stream to contain pure hydrogen product permeated through the outer membrane tube and with the exit reject stream from the permreactor which contains product alkenes and non-permeate hydrogen and unreacted alkanes, to be passed through a heat exchanger to reduce its temperature by generating steam in other side of the exchanger which is used as feed into any steam requiring process with the exit from the heat exchanger alkenes, alkanes and hydrogen mixture to be entered into a membrane permeator wherein the membrane is made by one of the following materials:

organic polymer membrane, inorganic membrane, composite inorganic-metal-organic membrane composite inorganic-organic membrane composite metal-organic membrane metal or metal alloy membrane non-porous inorganic membrane carbon membrane

which all materials are permselective to hydrogen only, and separate hydrogen in permeate stream from the unreacted alkanes and product alkenes, which exit from the non-permeate side of the permeator as a reject stream to be used for

polyolefin synthesis in consecutive polymerization reactors,

oxygenated compound synthesis in consecutive synthesis reactors,

including ethylene glycol, ethylene oxide, propylene glycol, propylene oxide, ethanol, propanol, isopropanol, with the hydrogen product recovered in the permeate stream of the permeator to be used as single hydrogen stream or as combined hydrogen stream after its combination with the hydrogen stream permeated through the first permeable reactor, in

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chemical synthesis, and in fuel type reactions,

including use as feedstock to hydrogenation reactors for methanol, ammonia, and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

The process of claim 9, as applies to dehydrogenation reactions of alkanes, with 31. the feed to consist of pure or mixture of alkanes which are saturated hydrocarbons and react in the catalytic zone of the permreactor, with hydrogen and unsaturated alkenes to be produced via reversible dehydrogenation reactions, with the final permeate stream to contain pure hydrogen product permeated through the multiple inner polymer membrane tubes, and with the exit reject stream from the permreactor which contains alkenes and non-permeate hydrogen as products and unreacted alkanes, to be passed through a heat exchanger to reduce its temperature by generating steam in other side of the exchanger which is used as feed into any steam requiring process with the exit from the heat exchanger alkenes, alkanes and hydrogen mixture to be entered into a membrane permeator wherein the membrane is made by one of the following materials:

organic polymer membrane, inorganic membrane, composite inorganic-metal organic membrane composite inorganic-organic membrane composite metal-organic membrane metal or metal alloy membrane non-porous inorganic membrane carbon membrane

which all materials are permselective to hydrogen only, and separate hydrogen in permeate stream from the unreacted alkanes and product alkenes, which exit from the non-permeate side of the permeator as a reject stream to be used for

polyolefin synthesis in consecutive polymerization reactors,

oxygenated compound synthesis in consecutive synthesis reactors,

including ethylene glycol, ethylene oxide, propylene glycol, propylene oxide, ethanol, propanol, isopropanol, with the hydrogen product recovered in the permeate stream of the permeator to be used as single hydrogen stream or as combined hydrogen stream after its combination with the hydrogen stream permeated through the first permeable reactor, in

chemical synthesis,

and in fuel type reactions,

including use as feedstock to hydrogenation reactors for methanol, ammonia, and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

The process of claim 29 wherein the alkane hydrocarbon is a single constituent or 32. a mixture of constituents of the following components:

ethane, propane,

n-butahe. i-butane. natural gas rich in ethane natural gas rich in propane refinery gas rich in ethane refinery gas rich in propane refinery gas rich in butane refinery gas/rich in isobutane refinery gas tich in ethane, propane, butane, isobutane.

The process of claim 29 wherein the membrane in permeator is made from an 33. organic polymer or composite or copolymer of organic polymers selected from the group of

polyimides, polycarbonates, polysulfones, polybenziim\dazoles, polyphosphazenes, polyamides, polystyrenes, polycaprolactams, parylenes, polyvinyl halides, polyacetates, polysiloxanes

or from inorganic-organic composite materials made by a mixture of one or more of the above polymers with one or more of the following ceramic oxides:

alumina (Al_2O_3) , titania (TiO₂), silica (SiO₂), zirconia (ZrO₂)

or from metal and metal alloys materials comprising by one or more of the following metals:

Palladium (Pd), Vanadium (V), Platinum (Pt), Silver (Ag), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni).

The process of claim 12 wherein the feed stream into the first permreactor 34. consists only of a hydrocarbon and steam (H2O(g)) mixture or an alcohol and steam mixture, reacting over a bed of metallic catalyst to produce H2, CO2 and traces of CO via

ľU M the reversible hydrocarbon steam reforming and water gas shift reactions, or alcohol steam reforming and water gas shift reactions, with hydrogen to permeate through the most-inner metal membrane tube and with the remaining components including unreacted hydrocarbons, alcohols, steam, carbon dioxide, carbon monoxide, and non-permeate hydrogen to exit through the reject stream of the outer cylinder.

- 35. The process of claim 34 with the reject stream from the permeator containing non-permeate unreacted hydrocarbons and product CO or unreacted alcohols and CO to be recycled into the inlet of first permeable reformer for continuous hydrocarbon-steam reforming and water gas shift reactions or alcohol steam reforming reactions into the catalytic zone of the outer cylinder.
- 36. The process of claim 34 with the reject stream from the permeator containing non permeate unreacted hydrocarbons and CO or alcohols and CO to enter into a consecutive placed reformer to react with steam over a bed of metallic catalyst via the steam reforming and water gas shift reactions and be converted into H₂, CO₂ product mixture, having the exit stream from last reforming reactor to condense its unreacted steam by passage through a heat exchanger and by generating new steam in other side of the heat exchanger to be used as feed in the inlet of the last reformer in an autothermic type operation, having the final exit dry mixture of H₂ and CO₂ from last heat exchanger to be combined with the permeate from the membrane permeator H₂ and CO₂ stream, to make a combined stream for use as feed in a methanol synthesis reactor and molten carbonate fuel cell unit, also in other

chemical synthesis and fuel type reactions either as it is mixture or after the CO₂ condensation and removal, as pure hydrogen, either

as a single hydrogen stream or as combined hydrogen stream after its combination with the hydrogen stream permeated from the first permeable reforming reactor.

wherein the membrane permeator following the 12 The process of claim 37. permeable reformer is replaced by a cryogenic separator, which operates at a cryogenic subzero temperature of absolute value higher than the condensation temperature of the unreacted steam, hydrocarbons, carbon dioxide, and lower than the condensation temperature of carbon monoxide and hydrogen, with the hydrogen and carbon monoxide gases to be separated as gases from the cryogenic separator, and with the steam, hydrocarbons and carbon dioxide to be separated as condensed liquids, with these liquified components to be continuously\or\periodically reheated by use of an immersed or surrounding heater to the section of the separator containing the liquified phase, and to be exited from the separator by use of a special valve, and be recycled into the inlet of the reforming reactor for continuous steam and carbon dioxide reforming and water gas shift reaction in the reformer, with the separated hydrogen and carbon monoxide mixture from the cryogenic separator to be used in following applications

methanol synthesis,

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gasoline synthesis via Fischer-Tropsch synthesis route, as combustion fuel in gas turbines and gas engines, as fuel in solid oxide fuel cells,

either as is mixture, or after mixing with all or part of the hydrogen stream permeated from the permeable reformer.

The process of claim 22 wherein the membrane permeator following the 38. permeable reformer is replaced by a cryogenic separator, which operates at a cryogenic subzero temperature of absolute value higher than the condensation temperature of the steam, hydrocarbons, carbon dioxide, and lower than the condensation temperature of carbon monoxide and hydrogen, with the hydrogen and carbon monoxide gases to be separated as gases from the cryogenic separator, and with the steam, hydrocarbons and carbon dioxide to be separated as condensed liquids, with these liquified components to be continuously or periodically reheated by use of an immersed or surrounding heater to the section of the separator containing the liquified phase, and to be exited from the separator by use of a special valve, and be recycled into the inlet of the reforming reactor for continuous steam and carbon dioxide reforming and water gas shift reaction in the reformer, with the separated hydrogen and carbon monoxide mixture from the cryogenic separator to be used in following applications

methanol synthesis, gasoline synthesis via Fischer-Tropsch synthesis route, as combustion fuel in gas turbines and gas engines, as fuel in solid oxide fuel cells,

either as is mixture, or after mixing with all or part of the hydrogen stream permeated from the permeable reformer.

The process of claim 11 wherein the membrane permeator following the 39. permeable reformer is replaced by a dryogenic separator, which operates at a cryogenic subzero temperature of absolute value higher than the condensation temperature of the unreacted steam, hydrocarbons, carbon dioxide, and lower than the condensation temperature of carbon monoxide and hydrogen, with the hydrogen and carbon monoxide gases to be separated as gases from the cryogenic separator, and with the steam, hydrocarbons and carbon dioxide to be separated as condensed liquids, with these liquified components to be continuously reheated by use of an immersed or surrounding heater to the section of the separator containing the liquified phase, and to be exited from the separator by use of a special valve, and be entered into the inlet of a consecutive reforming reactor for continuous steam and carbon dioxide reforming and water gas shift reaction in the reformer and conversion into H2 and CO2 products, having the exit stream from the last reforming reactor to condense its unreacted steam by passage through a heat exchanger and by generating new steam in the other side of the heat exchanger to be used as additional steam feed in the inlet of this last reforming reactor in an autothermic type operation, having the final exit dry mixture of H₂\and CO₂ from last heat exchanger to be used as direct feed in a methanol synthesis reactor and molten carbonate fuel cell unit, also in other

chemical synthesis

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and fuel type reactions

either as it is mixture or after the CO₂ condensation and removal, as pure hydrogen, moreover with the separated hydrogen and carbon monoxide mixture from the cryogenic separator to be used in following applications,

methanol synthesis,

gasoline synthesis via Fischer-Tropsch synthesis route,

as combustion\fuel in gas turbines and gas engines,

as fuel in solid pxide fuel cells,

either as is mixture, on after mixing with part or all of the hydrogen stream permeated from the first permeable reformer.

- The process of claim 5 as applied to the carbon dioxide and steam reforming of 40. hydrocarbons or carbon dioxide only reforming of hydrocarbons, wherein complete conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer and the reject exit stream from the reformer consists only of hydrogen and carbon monoxide products and unreacted and produced steam, which exit reject stream enters as a fuel feed in a solid oxide fuel cell unit for electric current generation, with part or all of the permeate hydrogen out of the permreactor to be recycled into the reject stream to complement for hydrogen fuel entering into the fuel cell.
- The process of claim as applied to the carbon dioxide and steam reforming of 41. hydrocarbons or carbon dioxide only reforming of hydrocarbons, wherein complete conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer and the reject exit stream from the reformer consists only of hydrogen and carbon monoxide products and unreacted and produced steam, which exit reject stream enters as a fuel feed in a solid oxide fuel cell unit for electric current generation, with part or all of the permeate hydrogen out of the permreactor to be recycled into the reject stream to complement for hydrogen fuel entering into the fuel cell.
- The process of claim 5 as applied to the carbon dioxide and steam reforming of 42. hydrocarbons or carbon dioxide reforming of hydrocarbons, wherein complete conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer and the reject exit stream from the reformer consists only of hydrogen and carbon monoxide products and unreacted and produced steam, which stream enters into a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming or water gas shift reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry cooled exit gas mixture to enter into a membrane permeator made by one of the following materials:

organic polymer membrane, inorganic membrane composite inorganic-metal-organic membrane, composite organic-inorgania membrane, composite organic-metal membrane,

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metal on mtal-alloy membrane, non-porous inorganic membrane, carbon membrane,

which all materials are permselective to hydrogen, and separate hydrogen in permeate stream from carbon monoxide product which exit from the non-permeate side of the permeator as a reject stream, with the separated hydrogen gas from the permeator and the permeable reforming reactor to be used in

chemical synthesis

and fuel type reactions

including hydrogen feed in hydrogenation reactors for methanol, ammonia and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types, and with the rejected CO containing stream from the permeator to be used in

methanol and gasoline hydrocarbons synthesis,

as fuel feed in solid oxide fuel cells,

as feed in a consecutive water gas shift reactor for production of H2 and CO2.

The process of claim 5 as applied to the carbon dioxide and steam reforming of 43. hydrocarbons or carbon/dioxide only reforming of hydrocarbons, wherein high enough conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer, so that reject exit stream from the reformer contains non-permeate hydrogen product, carbon monoxide product, traces of unreacted hydrocarbons and carbon dioxide, and unreacted and produced steam, which stream enters into a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming or water gas shift reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content,/with the dry\exit gas mixture to enter into a methanol synthesis catalytic reactor which produces methanol in the gas or liquid phase by reacting hydrogen and carbon monoxide over a metallic catalyst, with the methanol product stream to exit from the synthesis reactor and with a part or all of it to be used as fuel feed in a methanol driven fuel cell, also with a part of it to be fed in a consecutive methanol steam reforming catalytic reactor wherein methanol reacts with steam over a bed of metallic catalyst via the methanol decomposition reaction to hydrogen and carbon monoxide and the parallel water gas shift reaction to hydrogen and carbon dioxide, with final reaction products to be hydrogen and carbon dioxide which together with unreacted steam exit from the last methanol steam reforming reactor and passes through a heat exchanger to condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the two reforming reactors, with the exit stream from the heat exchanger to contain only hydrogen and carbon dioxide which is used as feed in molten carbonate fuel cells, or after the CO2 condensation and removal, pure hydrogen is recovered and used as feed in hydrogenation reactors for methanol, ammonia and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

The process of claim 1 as applied to the carbon dioxide and steam reforming of 44. hydrocarbons of carbon dioxide only reforming of hydrocarbons, wherein high enough conversion of hydrocarbons and carbon dioxide occurs in the permeable reformer, so that reject exit stream from the reformer contains non-permeate hydrogen product, carbon monoxide product, traces of unreacted hydrocarbons and carbon dioxide, and unreacted and produced steam, which stream enters into a heat exchanger to reduce its temperature and condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the first reforming reactor and any subsequently placed steam reforming or water gas shift reactor, with the exit stream from the heat exchanger to be passed through a bed of moisture adsorbing particles to remove any moisture content, with the dry exit gas mixture to enter into a methanol synthesis catalytic reactor which produces methanol in the gas or liquid phase by reacting hydrogen and carbon monoxide over a metallic catalyst, with the methanol product stream to exit from the synthesis reactor and with a part or all of it to be used as fuel feed in a methanol driven fuel cell, also with a part of it to be fed in a consecutive methanol steam reforming catalytic reactor wherein methanol reacts with steam over a bed of metallic catalyst via the methanol decomposition reaction to hydrogen and carbon monoxide and the parallel water gas shift reaction to hydrogen and carbon dioxide, with final reaction products to be hydrogen and carbon dioxide which together with unreacted steam exit from the last methanol steam reforming reactor and passes through a heat exchanger to condense the containing steam by generating new steam in other side of the exchanger which is used as feed into the two reforming reactors, with the exit stream from the heat exchanger to contain only hydrogen and carbon dioxide which is used as feed in molten carbonate fuel cells, or after the CO condensation and removal, pure hydrogen is recovered and used as feed in hydrogenation reactors for methanol, ammonia and gasoline hydrocarbon synthesis, also in gas turbines, engines, and fuel cells of proton exchange membrane, alkaline, molten carbonate, solid oxide and phosphoric acid types.

45. The process of claim 43 wherein a part or all of the product stream of hydrogen and carbon dioxide mixture exiting from the last methanol steam reforming reactor is recycled as side feed into the methanol synthesis reactor, and wherein a part or all of the permeate hydrogen stream coming out of the first permeable reformer is recycled as well as side feed into the methanol synthesis reactor, so that a combined mixture of hydrogen, carbon monoxide and carbon dioxide is used within this catalytic reactor for increasing the efficiency of methanol synthesis.

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